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*On the Chemical Examination of certain Indian Food Stuffs. Part I, Fats and Oils.*—By P. C. RAY, D. SC. Communicated by ALEX. PEDLER, F.R.S.

[Read February 7th.]

Of late years a belief has been gaining ground in Calcutta, Bombay and in many other important towns in India, not apparently without reason, that wholesale adulteration is practised in many of the common articles of diet, notably in ghee, butter, milk, mustard oil, &c. The present investigation was undertaken with a view to throw some light on these points, and it embodies the results of work carried on at intervals during the last four years.

#### PRELIMINARY.

As butter enters largely into the dietary of the people of Europe and America, abundant work has been done by Chemists on its analysis. It is, however, well-known that the composition of milk and of the butter made from it is, within certain limits, dependent on the breed, climate, method of feeding the cows, period of lactation, and so on. The standard for genuine butter as generally accepted in England, especially at Somerset House, cannot therefore be always accepted as a safe guide in this country.

The analysis of the fixed oil of mustard and the various other oils with which it is generally sophisticated also presents considerable difficulties. Not much work has been done in this field. The history of the substances which have been subjected to analysis is seldom given, and the experimental methods are not generally described in sufficient detail to enable the results to be compared. While the information available is meagre on the one hand, the results published from time to time are in themselves in some cases contradictory. It was thus found to be

necessary to work out in the first instance a series of *constants* for such Indian food-stuffs as mustard oil, butter, ghee, &c., which might be of some help in deciding cases of falsification.

Particular care was taken in procuring genuine samples of the substances. The oils were, in many cases, expressed under direct supervision from seeds carefully selected, so that the purity of the products was unquestionable. A sample of pure mustard oil was also obtained through the courtesy of the Superintendent, Alipur Jail, and another of coconut oil from the officer in charge of the "Copra" works, Viper Island, Port Blair, with a certificate from him, guaranteeing its purity, and stating it to be a standard sample.

The preliminary examination of the fats and oils is much helped by the determination of certain physical *constants*, *e. g.*, melting point, specific gravity, index of refraction, &c. The work in the present communication is confined solely to the chemical methods. The application of the physical tests, is reserved for a future occasion.

The fats and oils are simply combinations of certain acids, the so-called fatty acids, *e. g.*, butyric, stearic, oleic, palmitic, &c., with glycerin; hence they have been named the *glycerides*. By estimating the amount of both or either of these constituents of fatty substances, valuable information is obtained as to their nature. Now, if a fat be treated with an alkali, the fatty acids contained in it combine with the alkali, resulting in the formation of organic salts, commonly called a *soap*, and the separation of glycerin. It so happens, however, that the molecular weights of some of these fatty acids vary within wide limits. Thus, butyric acid, occurring in butter-fat has a molecular weight equivalent to 88, while erucic acid, a component of mustard oil, has a molecular weight of 338. A molecule of caustic potash weighing 56, will exactly neutralise 88 parts by weight of butyric acid or 338 parts by weight of erucic acid. Hence a given weight of butter-fat will require a far larger proportion of caustic potash to convert it into soap—to *saponify* it, as it is technically called—than the same weight of mustard oil. Koettstorfer has made use of this principle. It has in fact been found by actual experiments that while 100 grammes of butter-fat require very nearly 22 grammes of caustic potash for saponification, the same weight of mustard oil requires only 17 grammes of the alkali. The amount of glycerin in a fat or oil also will vary in a corresponding manner.

Again butyric, caproic and other volatile acids present in cocoa-nut oil, butter-fat, &c., may be easily separated from the non-volatile acids by distillation, and their amount ascertained by their potash neutralising power. Upon this principle is based the well-known Reichert's

test. The amount of iodine absorbed by different fats and oils also lies within wide ranges. The iodine absorption test has been employed with remarkable success by Baron Hübl in deciding cases of adulteration.

The following processes have been made use of:—

1. Direct titration of the fats and oils by alcoholic potash—  
Koettstorfer's test.
2. Estimation of the amount of glycerin.
3. Iodine absorption test of Hübl.
4. Estimation of the volatile fatty acids—Reichert's test.

The detailed results obtained by each of these methods as applied in the present inquiry will now be described.

#### KOETTSTORFER'S METHOD.

Most of the oils, when recently expressed, contain suspended impurities derived from the seeds, &c., in a very fine state of division. These settle down in course of time. The oils thus clarified by subsidence were filtered through bibulous paper to remove any traces of adherent moisture which might be present. The application of even a gentle heat cannot be resorted to for this purpose. Mustard oil, which is classed among the non-drying oils, was found to gain in weight continually when placed inside the chamber of a water-oven and weighed at intervals of 15 to 20 minutes.

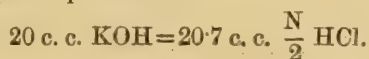
PREPARATION OF ALCOHOLIC POTASH.—The alcoholic solution of potash, approximately of semi-normal strength was prepared by dissolving sticks of potash in pure alcohol. The solution, filtered off the insoluble residue, is generally found to have a reddish-yellow color. It has therefore to be decolorised by shaking with pure animal charcoal.

#### OIL OF MUSTARD.

*Sinapis nigra*, *S. alba* (Nat. order—Cruciferae.)

Different samples of mustard seeds were found to yield a fixed oil varying from 32% to 36% of the air-dried seeds.

1. 2.534 gm. oil were weighed into a bottle of about 12 oz. capacity, and 20 c. c. of alcoholic potash solution were added. The mouth of the bottle was closed with an India-rubber cork, fastened by means of wire. The bottle was kept immersed in boiling water for 45 minutes. A blank experiment under exactly similar conditions was made side by side to determine the strength of the potash. The indicator used was phenolphthalein—



4.95 c. c.  $\frac{N}{2}$  HCl were required to neutralise the excess of alkali.

(20.7 - 4.95) c. c. or 15.75 c. c.  $\frac{N}{2}$  HCl represent the amount of alkali required for the saponification of the oil.

$$1 \text{ c. c. } \frac{N}{2} \text{ HCl} = 0.02805 \text{ gm. KOH}$$

Amount of potash consumed by 1,000 gm. oil (=saponification equivalent), is therefore equal to  $\frac{15.75 \times 0.02805 \times 1000}{2.534}$  gm. = 174.5 gm.

2. 1.713 gm. oil were heated in a flask over a water-bath for ten minutes with 20 c. c. KOH solution, the mouth of the flask being covered by a watch-glass—

$$20 \text{ c. c. KOH} = 20.7 \text{ c. c. } \frac{N}{2} \text{ HCl (Blank experiment)}$$

10.1 c. c.  $\frac{N}{2}$  HCl were required by the excess of potash.

$$\text{Saponification equivalent} = \frac{10.6 \times 0.02805 \times 1000}{1.713} = 173.5$$

3. Mustard oil expressed from a different sample of seeds.

3.084 gm. oil were treated with 20 c. c. KOH solution in a bottle, which was immersed in boiling water for about 40 minutes; the mouth of the bottle being closed by an India-rubber cork tied down by means of wire—

$$20 \text{ c. c. KOH} = 20.8 \text{ c. c. } \frac{N}{2} \text{ HCl (Blank titration)}$$

1.5 c. c.  $\frac{N}{2}$  HCl were required for the excess of potash.

or 19.3 c. c.  $\frac{N}{2}$  HCl represented the amount of alkali used up.

$$\text{Saponification equivalent} = \frac{19.3 \times 0.02805 \times 1000}{3.084} = 175.5$$

4. 2.222 gm. oil were treated with 20 c. c. KOH solution and heated in a flask over a water-bath for 12 minutes; the mouth of the flask being covered with a watch-glass—

$$\text{Excess of alkali required } 7 \text{ c. c. } \frac{N}{2} \text{ HCl}$$

20 c. c. KOH     ,,     20.8     ,,     ,,     (Blank titration).

$$\text{Saponification equivalent} = \frac{13.8 \times 0.02805 \times 1000}{2.222} = 174.2$$



5. 1.8012 gm. oil were saponified under the same conditions as described above, with 40 c. c. KOH solution—

$$40 \text{ c. c. KOH} = 32.0 \text{ c. c. } \frac{N}{2} \text{ HCl}$$

$$\text{Excess of alkali} = 21.0 \text{ ,, ,,}$$

$$\text{Saponification equivalent} = \frac{0.02805 \times 11 \times 10^3}{1.8012} = 171.3$$

6. Pure mustard oil from Alipur Jail.

3.493 gm. oil were mixed with 20 c. c. potash solution and the mixture kept immersed in boiling water for over half-an-hour. The mouth of the bottle being closed by a cork fastened by a wire—

$$20 \text{ c. c. KOH} = 30.7 \text{ c. c. } \frac{N}{2} \text{ HCl}$$

$$\text{Excess of alkali} = 9.2 \text{ ,, ,,}$$

$$\text{Saponification equivalent} = \frac{21.5 \times 0.02805 \times 10^3}{3.493} = 172.7$$

7. Duplicate analysis of the above. 2.195 gm. oil heated to boiling on a water-bath with 20 c. c. KOH solution for 15 minutes, the mouth of the flask being covered with a watch-glass.

$$20 \text{ c. c. KOH} = 30.7 \text{ c. c. } \frac{N}{2} \text{ HCl (Blank experiment)}$$

$$\text{Excess of alkali} = 17.2 \text{ ,, ,,}$$

$$\text{Saponification equivalent} = \frac{13.5 \times 0.02805 \times 10^3}{2.195} = 172.5$$

It would thus appear that mustard oil is very easily saponified by alcoholic potash, and that a large excess of the latter is not necessary.

The oil was in some cases found to have a pale yellow color, in others the tint was somewhat deeper. The soap solutions were tinged accordingly. The want of exact uniformity in the tint sometimes interfered with the exact determination of the conclusion of the reaction during the titrations. It may also be stated that the soap solutions were generally diluted with about 25 c. c. of hot water, from which all traces of carbonic acid gas had been driven off by boiling.

In the above experiments it will be seen that the saponification equivalent of the samples of mustard oil has varied between 175.5 and 171.3, the average of the seven determinations being 173.5.

Hence it would be safe probably to adopt the saponification equivalent of mustard oil as lying between 171—175.

## SAPONIFICATION EQUIVALENT FOR NIGER-SEED OIL.

*Guizotia abyssinica* (Nat. ord.—Compositæ).

As this oil is one of the commonest adulterants of mustard oil, a genuine sample of it was procured for experiments.

1. 1.4605 gm. oil were weighed out into a flask, 20 c. c. of alcoholic potash were then added, the mixture covered with a watch-glass and treated to gentle boiling, with occasional agitation for 15 minutes.

$$20 \text{ c. c. KOH} = 15.95 \text{ c. c. } \frac{N}{2} \text{ HCl (Blank experiment)}$$

$$\text{Excess of alkali} = 6.1 \text{ ,, ,,}$$

$$\text{Saponification equivalent} = \frac{9.85 \times 0.02805 \times 10^3}{1.4605} = 189.2$$

2. 1.906 gm. oil were saponified as above with 40 c. c. alcoholic potash.

$$40 \text{ c. c. KOH} = 31.9 \text{ c. c. } \frac{N}{2} \text{ HCl}$$

$$\text{Excess of alkali} = 18.8 \text{ ,, ,,}$$

$$\text{Saponification equivalent} = \frac{13.1 \times 0.02805 \times 10^3}{1.906} = 192.8$$

3. 2.184 gm. oil were treated as above with 40 c. c. alcoholic potash solution.

$$40 \text{ c. c. KOH} = 31.8 \text{ c. c. } \frac{N}{2} \text{ HCl (Blank experiment)}$$

$$\text{Excess of alkali} = 17.0 \text{ ,, ,,}$$

$$\text{Saponification equivalent} = \frac{14.8 \times 0.02805 \times 10^3}{2.184} = 190.0$$

The determinations described above were made in November 1891, when the oil was fresh. It was preserved in a stoppered bottle and a year after (November 1892) the saponification equivalent was found to be 191.6.

The saponification number for niger-seed oil may be taken as 190.

## SAPONIFICATION EQUIVALENT FOR COCOANUT OIL.

The sample was obtained from Viper Island, Port Blair, and was guaranteed to be a "standard sample."

1. 1.275 gm. oil were treated with 20 c. c. alcoholic solution and heated to boiling on the water-bath as in the previous cases.

$$20 \text{ c. c. KOH} = 30.45 \text{ c. c. } \frac{N}{2} \text{ HCl (Blank experiment)}$$

$$\text{Excess of alkali} = 18.75 \text{ ,, ,,}$$

$$\text{Saponification equivalent} = \frac{11.7 \times 0.02805 \times 10^3}{1.275} = 257.4$$

2. 1.24 gm. oil were treated with 20 c. c. alcoholic potash as above  
 20 c. c. KOH = 30.4 c. c.  $\frac{N}{2}$  HCl (Blank experiment)

Excess of alkali = 19.0 " "

$$\text{Saponification equivalent} = \frac{11.4 \times 0.02805 + 10^3}{1.24} = 257.8$$

3. 1.038 gm. oil with 20 c. c. alcoholic potash solution.

20 c. c. KOH = 20.4 c. c.  $\frac{N}{2}$  HCl

Excess of alkali = 10.8 " "

$$\text{Saponification equivalent} = \frac{9.6 \times 0.2805 \times 10^3}{1.038} = 259.4$$

The saponification equivalent for cocoanut oil is thus found to lie between 257—260.

#### SAPONIFICATION EQUIVALENT OF PURE FRESH GHEE (CLARIFIED BUTTER).

1. 13.525 gm. ghee were heated in a water-oven and then kept inside a desiccator for a week. The ghee was then found to weigh 13.5 gm. It would thus appear that ghee is not hygroscopic; nor does it contain any moisture.

1. 1.8196 gm. ghee were treated with 20 c. c. alcoholic potash solution. Details as in the previous cases.

20 c. c. KOH = 31.0 c. c.  $\frac{N}{2}$  HCl (Blank titration)

Excess of alkali = 16.55 " "

$$\text{Saponification equivalent} = \frac{14.45 \times 0.02805 \times 10^3}{1.8196} = 222.7$$

2. 2.0776 gm. ghee saponified with 20 c. c. alcoholic potash solution.

20 c. c. KOH = 30.8 c. c.  $\frac{N}{2}$  HCl (Blank titration)

Excess of alkali = 14.5 " "

$$\text{Saponification equivalent} = \frac{16.3 \times 0.02805 \times 10^3}{2.0776} = 220.07$$

3. The same ghee re-melted and filtered. There was no residue on the filter.

1.294 gm. saponified with 20 c. c. alcoholic potash.

20 c. c. KOH = 30.9 c. c. =  $\frac{N}{2}$  HCl (Blank titration)

Excess of alkali = 21.45 " "

$$\text{Saponification equivalent} = \frac{9.45 \times 0.02805 \times 10^3}{1.204} = 220.1$$

## ANOTHER SAMPLE OF GHEE.

1. 1.547 gm. were treated with 20 c. c. alcoholic potash, the mouth of the flask was closed with a cork to which was attached a long glass tube, which acted as a reflex condenser.

$$20 \text{ c. c. KOH} = 16.5 \text{ c. c. } \frac{N}{2} \text{ HCl (Blank tit.)}$$

$$\text{Excess of alkali} = 4.5 \text{ ,,}$$

$$\text{Saponification equivalent} = \frac{12 \times 0.02805 \times 10^3}{1.547} = 217.6$$

2. 1.1512 gm. ghee treated with 30 c. c. potash.

$$30 \text{ c. c. KOH} = 25 \text{ c. c. } \frac{N}{2} \text{ HCl (Blank tit.)}$$

$$\text{Excess of alkali} = 16.0 \text{ ,,}$$

$$\text{Saponification equivalent} = \frac{9 \times 0.02805 \times 10^3}{1.1512} = 219.2$$

## SAPONIFICATION EQUIVALENT FOR MOWA "BUTTER."

Oil of *Bassia latifolia*—(Nat. order—Sapotaceæ.)

This substance by its physical characters, *e. g.*, color, consistency, melting point, &c., much resembles ghee, and is therefore frequently used for its falsification.

1. 1.396 gm. oil were placed in a stout 12oz. bottle, together with 40 c. c. alcoholic potash solution. The mouth of the bottle was closed with a India-rubber cork, fastened by means of wire. It was then kept immersed in boiling water, with occasional shaking.

40 c. c. alcoholic potash were also heated under exactly the same conditions—

$$40 \text{ c. c. KOH} = 31.6 \text{ c. c. } \frac{N}{2} \text{ HCl (Blank exp.)}$$

$$\text{Excess of alkali} = 21.6 \text{ ,,}$$

$$\text{Saponification equivalent} = \frac{10 \times 0.02805 \times 10^3}{1.396} = 200.9$$

2. 2.086 gm. oil heated under pressure just as above—

$$20 \text{ c. c. KOH} = 29.3 \text{ c. c. } \frac{N}{2} \text{ HCl (Blank.)}$$

$$\text{Excess of alkali} = 14.6 \text{ ,,}$$

$$\text{Saponification equivalent} = \frac{14.7 \times 0.02805 \times 10^3}{2.086} = 197.6$$

The soap solutions were perfectly clear and colourless.

To ensure complete saponification it is preferable to treat Mowa oil under pressure as above. If the oil be simply heated on a water-



bath, with a watch-glass at the mouth of the flask, the soap solution is sometimes found to have a turbid appearance, and the Saponification equivalent comes out rather low.

#### SAPONIFICATION NUMBER FOR MUTTON-FAT.

The fat was melted over a water-bath and filtered to get rid of the shreds of membrane, &c.

1. 1.3906 gm. of fat were treated with 20 c. c. alcoholic potash and heated over a water-bath for 15 minutes.

$$20 \text{ c. c. KOH} = 16.2 \text{ c. c. } \frac{N}{2} \text{ HCl (Blank.)}$$

$$\text{Excess of ,,} = 6.0 \text{ ,, ,,}$$

$$\text{Saponification equivalent} = \frac{0.02805 \times 10.2 \times 10^3}{1.3906} = 205.7$$

2. 0.9318 gm. of the same sample treated with 20 c. c. alcoholic potash, &c.

$$20 \text{ c. c. KOH} = 16.15 \text{ c. c. } \frac{N}{2} \text{ HCl (Blank.)}$$

$$\text{Excess of ,,} = 9.3 \text{ ,, ,,}$$

$$\text{Saponification equivalent} = \frac{0.02805 \times 6.85 \times 10^3}{0.9318} = 206.2$$

#### ANOTHER SAMPLE OF MUTTON-FAT.

0.8354 gm. was treated with 20 c. c. KOH.

$$20 \text{ c. c. KOH} = 16.15 \text{ c. c. } \frac{N}{2} \text{ HCl (Blank.)}$$

$$\text{Excess of ,,} = 10.2 \text{ ,, ,,}$$

$$\text{Saponification equivalent} = \frac{5.95 \times 0.02805 \times 10^3}{0.8354} = 199.8$$

Duplicate analysis of the same sample gave the number as 199.2.

#### SAPONIFICATION EQUIVALENT OF OIL OF SESAME.\*

*Sesamum indicum* (Nat. Order: Pedaliaceæ.)

1. 1.6835 gm. oil were heated over a water-bath with 20 c. c. alcoholic potash solution for 15 minutes.

2. 1.3145 gm. oil were heated as above with 30 c. c. alcoholic potash solution.

$$20 \text{ c. c. KOH} = 16.2 \text{ c. c. } \frac{N}{2} \text{ HCl (Blank.)}$$

$$\therefore 30 \text{ c. c. ,,} = 24.3 \text{ ,, ,,}$$

\* The oil was extracted by means of carbon bisulphide.

4.8 c. c.  $\frac{N}{2}$  HCl were required by (1) for the excess of alkali.

15.4 „ „ „ „ (2) „ „ „ „

Saponification equivalent of (1) =  $\frac{11.4 \times 0.02805 \times 10^3}{1.6835} = 190.0$

Do. do. (1) =  $\frac{8.9 \times 0.02805 \times 10^3}{1.3145} = 189.9$

#### SAPONIFICATION EQUIVALENT OF LARD.\*

1. 1.4245 gm. lard were heated over a water-bath with 20 c. c. alcoholic potash solution.

2. 1.432 gm. lard heated as above with 30 c. c. alcoholic potash solution—

20 c. c. KOH = 15.8 c. c.  $\frac{N}{2}$  HCl

∴ 30 „ „ = 23.7 „ „

(1) Consumed 5.9 c. c.  $\frac{N}{2}$  HCl for the excess of alkali.

(2) „ 13.7 „ „ „ „

Saponification equivalent for (1) =  $\frac{9.9 \times 0.02805 \times 10^3}{1.4245} = 194.9$

„ „ „ (2) =  $\frac{10 \times 0.02805 \times 10^3}{1.432} = 195.9$

Mean of two = 195.4.

#### ESTIMATION OF GLYCERIN ACCORDING TO FOX AND WANKLYN'S METHOD, AS IMPROVED BY BENEDIKT AND ZSIGMONDY.

In view of the contradictory statements which have appeared from time to time as regards the applicability of this process, a few preliminary experiments were undertaken with the object of testing its trustworthiness:—

(a) A solution of pure oxalic acid was divided into two equal portions. The oxalic acid was thrown down by means of calcium acetate in presence of acetic acid. The oxalate precipitate was in one case dissolved in hot hydrochloric acid, the solution diluted with water and further acidified with sulphuric acid, warmed to about 60°, and titrated against accurately standardised permanganate solution. In another case the oxalate precipitate was converted by ignition into lime.

\* The lard was a standard sample and was not taken off any particular part of the pig's carcass.

(1 c. c.  $\frac{N}{10}$   $\text{KMnO}_4 = 0.0028$  gm.  $\text{CaO}$ ). The two results were found to be thoroughly concordant.

(b) Oxidation of glycerin to oxalic acid :—

1. 5.62 gm. of glycerin were weighed into a flask and diluted to 500 c. c. with water. 25 c. c. of the solution were oxidised to oxalic acid.\*

25 c. c. sol. =  $\frac{5.62}{20}$  gm. glycerin = 0.281 gm. glycerin on the supposition that the sample contained cent. per cent. of glycerin.

The potassium oxalate solution was made up to 500 c. c. of which 100 c. c. gave 0.028 gm.  $\text{CaO}$  (by ignition)

or 500 c. c.  $\text{K}_2\text{O}$  Sol. =  $0.028 \times 5$  gm.  $\text{CaO} = 0.02 \times 5$  Ca

But 0.002 gm. Ca = 0.0046 gm. glycerin.

∴ 0.02 gm. Ca = 0.046 gm. glycerin.

or  $(0.02 \times 5)$  gm. Ca =  $0.046 \times 5$  gm. glycerin = 0.23 gm. glycerin.

The Sample thus contained  $100 \times \frac{0.23}{0.281}$  or 81.8% of glycerin.

2. 5.895 gm. glycerin (the same sample) were dissolved in water and diluted to 500 c. c., of which 25 c. c. were oxidised to oxalic acid.

25 c. c. sol. =  $\frac{5.895}{20}$  gm. = 0.2947 gm. glycerin.

The oxalate solution was made up to 500 c. c., of which 100 c. c. yielded 0.0285 gm.  $\text{CaO} = 0.02035$  gm. Ca.

But 1 c. c.  $\frac{N}{10}$   $\text{KMnO}_4 = 0.002$  Ca from  $\text{CaC}_2\text{O}_4$   
 = 0.0046 gm. glycerin.

∴ 0.02035 gm. Ca = 0.046805 gm. glyc.

or 500 c. c. oxalate sol. =  $(0.046805 \times 5)$  gm. glyc.

∴ = 0.234 gm. glyc.

The sample thus contained  $100 \times \frac{0.234}{0.2947}$  or 79.75% glycerin.

The mean of the above two determinations may be taken as 80% approximately.

#### SAPONIFICATION OF MUSTARD OIL.

(Estimation of glycerin.)

1. 8.65 gm. oil were saponified according to Allen's method.† The soap solution was treated with dilute sulphuric acid, the beaker in

\* An abstract of Benedikt and Zsigmondy's method will be found in *Jour. Soc. Chem. Ind.* IV, 610.

† The use of alcoholic potash is highly objectionable; "pure methyl alcohol" is difficult to procure. "Hence," as Allen remarks, "I have latterly aimed at

which it was contained was immersed in ice-cold water to completely solidify the separated fatty acids. The glycerin solution was then filtered off and made up to 250 c. c. of which 20 c. c. were each time oxidised to oxalic acid. The oxalic acid was thrown down by calcium acetate. The precipitate of  $\text{Ca}\bar{\text{O}}$  was dissolved in  $\text{HCl}$ , further acidified with  $\text{H}_2\text{SO}_4$ , and titrated with  $\text{N}/10 \text{KMnO}_4$ . The strength of the permanganate solution was ascertained each time by titration against re-crystallised oxalic acid and sometimes against ferrous ammonic sulphate.

7.5 c. c.  $\text{N}/10 \text{KMnO}_4$  were used up by the oxalic acid solution.

1 c. c.  $\text{N}/10 \text{KMnO}_4 = 0.0063 \text{ gm. } \bar{\text{O}} = 0.0046 \text{ gm. glycerin}$ ; hence amount of glycerin in 20 c. c. sol.

$$= 0.0046 \times 7.5 \text{ gm.}$$

$\therefore$  Total glycerin in 250 c. c.

$$= (0.0046 \times 7.5) \times \frac{250}{20} \text{ gm.}$$

$$= 0.431 \text{ gm.}$$

Per cent. of glycerin in the oil = 4.98.

But the  $\text{N}/10 \text{KMnO}_4 = 0.0061 \text{ gm. } \bar{\text{O}}$  instead of 0.0063 gm.  $\bar{\text{O}}$ .

Per cent. of glycerin in the oil = 4.82.

2. 8.48 gm. oil were saponified just as above. The glycerin solution made up to 250 c. c., of which 50 c. c. were oxidised to oxalic acid.

The oxalate solution was divided into two equal portions, one-half (a) (= 25 c. c. glyc. sol.) was acidified with  $\text{H}_2\text{SO}_4$ , heated to boiling and titrated, the other half (b) was treated with  $\text{Ca } \bar{\text{A}}\text{c}$ , and the precipitated  $\text{Ca}\bar{\text{O}}$  dissolved in dilute  $\text{H}_2\text{SO}_4$  and then titrated with  $\frac{\text{N}}{10} \text{KMnO}_4$ .

(a) Required 17.0 c. c.  $\frac{\text{N}}{10} \text{KMnO}_4$

(b) ,, 15.0 ,, ,,

1 c. c.  $\frac{\text{N}}{10} \text{KMnO}_4 = 0.0046 \text{ gm. glyc.}$

15 c. c.  $\frac{\text{N}}{10} \text{KMnO}_4 = 0.0046 \times 15 \text{ gm. glyc.} = 0.069 \text{ gm. glyc.}$

$\therefore$  250 c. c. glyc. solution contains 0.69 gm. glycerin.

Per cent. of glycerin in the oil = 8.14.

Experience has shewn that the oxalate solution if titrated direct, after addition of  $\text{H}_2\text{SO}_4$ , gives the result too high. Precipitation of the

effecting saponification by aqueous alkali, and thus completely avoiding the source of error in question." *Jour. Soc. Chem. Ind.* V. 70; also Sutton's *Volumetric Analysis*, 6th ed. p. 345.



oxalate as  $\text{CaO}$  cannot be dispensed with. These experiences are in conformity with those of Allen and Belcher. Two more saponifications carried on as above yielded the percentage of glycerin as 5.3 and 6.0 respectively.

#### AN IMPROVED METHOD OF SAPONIFICATION.

It is thus evident that the saponification was by no means complete, as the percentage of glycerin ranged between 8.14 and 4.8. Allen's method had thus to be abandoned. It was, in fact, noticed that the oily layer invariably floated over the solution of caustic potash and that shaking simply brought about a momentary incorporation of the oil and alkali. The two layers separated as soon as the bottle was placed in the boiling water. This difficulty was obviated by the introduction into the bottle of asbestos wool, thoroughly ignited previously to get rid of accidental organic impurities. This absorbing medium brought the oil and the alkali into intimate contact with each other and thus complete saponification was ensured. The heating was done just as in the previous cases, *i. e.*, by immersion in boiling water.

1. 1.573 gm. oil were treated as above, the fatty acids liberated by means of dilute  $\text{H}_2\text{SO}_4$  and filtered off. The mass of asbestos, which had become slimy by the absorption of the fatty acids was then thrown on the filter-paper and repeatedly exhausted with hot water. Scarcely a trace of the fatty acids was found to pass through the filter-paper.\* The filtration was carried on with the aid of a Bunsen's pump.

The glycerin solution was made up to 250 c. c., of which 100 c. c. were oxidised to oxalic acid. The latter thrown down as  $\text{CaO}$ . The  $\text{CaO}$  dissolved in dilute  $\text{H}_2\text{SO}_4$  and the solution made up to 250 c. c., of which

$$100 \text{ c. c. reqd. } 4.7 \text{ c. c. } \frac{\text{N}}{10} \text{ KMnO}_4$$

$$\text{or } 250 \text{ ,, ,, } 11.75 \text{ ,, ,, } (=100 \text{ c. c. glycerin sol.)}$$

$$\therefore 250 \text{ c. c. glycerin solution} = 29.37 \text{ c. c. } \frac{\text{N}}{10} \text{ KMnO}_4$$

$$\text{and } 1 \text{ c. c. } \frac{\text{N}}{10} \text{ KMnO}_4 = 0.0046 \text{ gm. glyc.}$$

$$\therefore 29.37 \text{ ,, ,, } = 0.135102 \text{ gm. glyc.}$$

$$\text{or } 1.573 \text{ gm. oil yielded } 0.135102 \text{ gm. glyc.}$$

$$\text{whence glycerin } \frac{\circ}{\circ} = 8.6$$

2. 2.167 gram. oil were saponified as above.

The glycerin solution made up to 250 c. c. of which 100 c. c.

\* The filtered solution of glycerin was sometimes perfectly clear, sometimes slightly opalescent.

oxidised to  $\bar{O}$ , precipitated as  $\text{Ca}\bar{O}$ , &c., and titrated =  $16\cdot0$  c.  $\frac{N}{10} \text{KMnO}_4$

whence percentage of glycerin =  $8\cdot45$

3.  $1\cdot99$  gm. oil saponified as above. Details exactly the same as in the preceding.

$250$  c. c. glycerin solution =  $35$  c. c.  $\frac{N}{10} \text{KMnO}_4$

glycerin % =  $8\cdot1$

4.  $1\cdot3165$  gm. oil saponified according to the improved method. Details the same as in the previous cases—

$250$  c. c. glycerin sol. =  $25\cdot0$  c. c.  $\frac{N}{10} \text{KMnO}_4$

=  $0\cdot115$  gm. glycerin

glycerin % =  $8\cdot7$ .

The permanganate solution on direct titration against ferrous ammonium sulphate gave

$1$  c. c. =  $5\cdot6$  ( $1 - 0\cdot02$ ) mgs. Fe.

Whence glycerin per cent. (corrected) =  $8\cdot7$  ( $1 - 0\cdot02$ )

=  $8\cdot53$

5.  $2\cdot0365$  gm. oil saponified: details the same—

$250$  c. c. glyc. sol. =  $37\cdot5$   $\frac{N}{10} \text{KMnO}_4$

Glycerin per cent. =  $8\cdot33$  (corrected).

6.  $1\cdot264$  gm. oil saponified as above

$250$  c. c. glycerin solution =  $23\cdot75$  c. c.  $\frac{N}{10} \text{KMnO}_4$

Whence glycerin per cent. =  $8\cdot64$ .

It would thus be safe to take the percentage of glycerin in mustard oil as  $8\cdot5$ . The oil used was not in every case identical, but from different samples, in fact, the same as used in the determination of the saponification equivalent.

#### DETERMINATION OF GLYCERIN IN MUTTON-FAT BY THE ASBESTOS METHOD.

1.  $1\cdot0425$  gm. fat were saponified under pressure as in the case of mustard oil.

The glycerin solution was made up to  $500$  c. c. of which  $100$  c. c. were oxidised to  $\bar{O}$ . The  $\text{Ca}\bar{O}$  was dissolved in dilute  $\text{H}_2\text{SO}_4$  and made up to

$250$  c. c.;  $50$  c. c. of the latter were equivalent to  $1$  c. c.  $\frac{N}{10} \text{KMnO}_4$

or  $250$   $\text{Ca}\bar{O}$  sol. =  $100$  c. c. glyc. sol. =  $5$  c. c.  $\frac{N}{10} \text{KMnO}_4$

or 250 c. c. glycerin solution = 25 c. c.  $\frac{N}{10}$   $\text{KMnO}_4$

and 1 c. c.  $\frac{N}{10}$   $\text{KMnO}_4$  = 0.0046 gm. glycerin

Total amount of glycerin =  $0.0046 \times 25$  gm. = 0.115 gm.

whence percentage = 11.03.

But, 1 c. c.  $\frac{N}{10}$   $\text{KMnO}_4$  when titrated against pure oxalic acid was found to be equal to, 1 c. c.  $\frac{N}{10}$   $\text{KMnO}_4$  (1-0.02)

$\therefore$  per cent. of glycerin (corrected) =  $11.03 (1-0.02)$   
= 10.81.

2. 1.8877 gm. fat were saponified as above; the heating was continued for 6 days on an average of  $3\frac{1}{2}$  hours each day.

The filtrate\* (= glycerin solution) was made up to 500 c. c. of which 50 c. c. were oxidised to  $\text{K}\bar{\text{O}}$ , &c.

The  $\text{Ca}\bar{\text{O}}$  sol. was made up to 250 c. c. of which 100 c. c. required

1.7 c. c.  $\frac{N}{10}$   $\text{KMnO}_4$

$\therefore$  250 c. c.  $\text{Ca}\bar{\text{O}}$  sol. =  $(1.7 \times \frac{5}{2})$  c. c.  $\frac{N}{10}$   $\text{KMnO}_4$

or 50 c. c. glyc. sol. =  $4.25$  c. c.  $\frac{N}{10}$   $\text{KMnO}_4$

or 500 ,, ,, ,, = 42.5 ,, ,, ,,

whence percentage of glycerin = 10.36

per cent. corrected =  $10.36 (1-0.02)$  = 10.16

Theoretical percentage of glycerin in mutton-fat, calculated as tri-stearin = 10.33.

#### DETERMINATION OF GLYCERIN IN NIGER-SEED OIL.

1. 3.165 gm. oil were treated with potash solution and asbestos, &c., as in the case of mustard oil.

The glycerin solution was made up to 250 c. c. of which 50 c. c. were oxidised to  $\bar{\text{O}}$ , and the  $\text{Ca}\bar{\text{O}}$  sol. also made up to 250 c. c.—

50 c. c.  $\text{Ca}\bar{\text{O}}$  sol. = 3 c. c.  $\frac{N}{10}$   $\text{KMnO}_4$

\* The filtrate in the above cases was very faintly milky. It was therefore surrounded by ice-cold water to solidify, if possible, minute traces of fatty acids which might have remained in suspension. The opalescence, however, could not be got rid of. On standing for 3 to 4 days the solution kept in a stoppered flask became clear, but was at the same time the *nidus* of a kind of fungoid growth, resembling flakes of cotton-wool.

$$\therefore 250 \text{ c. c. CaO sol.} = 15 \text{ c. c. } \frac{N}{10} \text{ KMnO}_4$$

$$\text{or } 50 \text{ glycerin solution} = 15 \text{ ,, ,, ,,}$$

$$\text{or } 250 \text{ ,, ,, ,,} = 75 \text{ ,, ,, ,,}$$

$$\text{But } 1 \text{ c. c. } \frac{N}{10} \text{ KMnO}_4 = 0.0046 \text{ gm. glycerin.}$$

$$\text{Percentage of glycerin} = \frac{75 \times 0.0046 \times 10^2}{3.165} = 10.9.$$

2. 1.704 gm. oil were treated exactly as above, the glycerin solution made up to 500 c. c. of which 100 c. c. were oxidised to oxalic acid. The CaO dissolved in dilute  $\text{H}_2\text{SO}_4$  was made up to 250 c. c.

$$50 \text{ c. c. CaO sol.} = 1.6 \text{ c. c. } \frac{N}{10} \text{ KMnO}_4$$

$$\therefore 250 \text{ c. c. ,, ,,} = 8.0 \text{ ,, ,, ,,}$$

$$\text{or } 100 \text{ c. c. glycerin sol.} = 8.0 \text{ ,, ,, ,,}$$

$$\therefore 500 \text{ ,, ,, ,,} = 40.0 \text{ ,, ,, ,,}$$

$$\text{Percentage of glycerin} = \frac{40 \times 0.0046 \times 10^2}{1.704} = 10.8.$$

The percentage of glycerin in niger-seed oil is thus practically the same as in mutton-fat.

#### ESTIMATION OF GLYCERIN IN BUTTER-FAT.

The oxidation of glycerin by the alkaline permanganate is not applicable in the case of butter-fat, as the soluble fatty acids, *e. g.*, butyric, caproic, &c., it contains yield notable quantities of oxalic acid under the same treatment. The same remarks apply to the case of coconut oil (See *Chem. News*, Vol. LXIII, p. 251).

#### NOTE ON THE FOX AND WANKLYN METHOD OF ESTIMATING GLYCERIN.

This method, although it yields accurate results, can scarcely be made use of by the ordinary commercial analyst on account of its tedious and troublesome nature. Moreover, the manganese precipitate, sometimes bulky, cannot be properly washed without the aid of a Bunsen's filter-pump. The details recorded above will show that each determination of glycerin involves steady work of several hours. If ordinary alcohol be used as a solvent for the fats and oils, saponification is easily effected, but there is considerable risk of the loss of glycerin during the evaporation of alcohol.



## ON THE LOSS OF GLYCERIN BY VOLATILISATION.

2.165 gm. glycerin were diluted with water to 250 c. c.; 50 c. c. were each time mixed with 25 c. c. pure alcohol, the latter evaporated off on a water-bath in—

- (1) A platinum basin of 3 in. diameter.
- (2) A porcelain basin of 5 in. diameter.
- (3) Do. do. of about 3 in. diameter.

In (1) and (2) the percentage of glycerin was found to be 74.0; in (3) the percentage was 77.8. The percentage as found before (see p. 69) should have been 80.

It is thus evident that during the evaporation of alcohol considerable quantities of glycerin are carried off.

## IODINE ABSORPTION FOR FATS AND OILS.†

## COCONUT OIL.

The sample was the same as used for the determination of the saponification equivalent.

1. 1.3585 gm. oil were digested for 24 hours with 10 c. c. chloroform and 20 c. c. iodine solution. In this as well as in the subsequent analyses a blank experiment was each time made side by side, and under exactly similar conditions, to determine the strength of the iodine solution. The time allowed for digestion was from 18 to 24 hours.

20 c. c. iod. sol. + 10 c. c.  $\text{CHCl}_3$  = 35.0 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  (Blank exp.)  
 Excess of iodine = 27.5 " "  
 Diff. = 7.5 " "

7.5 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  represent the amount of iodine absorbed by the oil.  
 But 1 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  = 0.01265 gm. iodine.

Hence amount of iodine consumed by 100 gm. oil, "iodine degree,"  

$$= \frac{0.01265 \times 7.5 \times 100}{1.3585} = 6.99.$$

But the actual strength of the thiosulphate solution, as checked by titration against pure iodine, was found to be equal to 0.01265 (1-0.03) gm. per 1 c. c.

Corrected iodine number = 6.99 (1-0.03) = 6.78.

2. 1.459 gm. oil were digested as before.

26.5 cc  $\text{Na}_2\text{S}_2\text{O}_3$  sol. were taken up by the excess of iodine, and  
 20 c. c. iod. sol. = 35.0 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$ .

Iodine degree =  $\frac{0.01265 \times 8.5 \times 100}{1.459} = 7.37$

Corrected number = 7.37 (1-0.03) = 7.15

† For details of Hübl's method, see *Journ. Soc., Chem. Ind.* iii, 642 also Allen's *Org. Analysis*.

3. 1.016 gm. oil were digested for 24 hours with 20 c. c. 1 and 10 c. c.  $\text{CHCl}_3$

20 c. c. 1 + 10 c. c.  $\text{CHCl}_3 = 16.0$  c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  (Blank exp.)

Excess of iodine = 10.4 ,, ,,

Dif. = 5.6 ,, ,,

Iodine degree =  $\frac{0.01265 \times 5.6 \times 100}{1.016} = 6.97$

Corrected number =  $6.97 (1 - 0.03) = 6.76$ .

4. 1.984 gm. oil were digested with 30 c. c. iod. sol. and 10 c. c.  $\text{CHCl}_3$ .  
Excess of iodine = 13 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$ .

30 c. c. iod. sol. + 10 c. c.  $\text{CHCl}_3 = 24$  c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  (Blank exp.)

Iodine degree =  $\frac{0.01265 \times 11 = 100}{1.984} = 7.01$

Corrected number =  $7.01 (1 - 0.03) = 6.81$ .

#### GHEE (CLARIFIED BUTTER.)

1. 0.955 gm. ghee was digested for 24 hours with 10 c. c.  $\text{CHCl}_3$  and 20 c. c. iod. sol.

10 c. c.  $\text{CHCl}_3$  + 20 c. c. iod. sol. = 32.8 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$

Excess of iodine = 6.3 ,, ,,

Dif. = 26.5

Iodine degree =  $\frac{0.01265 \times 100 \times 26.5}{0.955} = 35.1$

2. 0.216 gm. ghee was digested as above  
27.0 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  was taken up by the excess of iodine.

Iodine degree =  $\frac{0.1265 \times 5.8 \times 100}{0.216} = 33.9$

Mean of the two determinations = 34.5

Corrected number =  $34.5 (1 - 0.03) = 33.5$

The saponification equivalent of this sample of ghee was found to be 221 (See p. 65).

#### ANOTHER SAMPLE OF GHEE.

1. 0.355 gm. was digested with 20 c. c. iod. sol. and 10 c. c.  $\text{CHCl}_3$ . 10.3 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  were required for the excess of iodine.

20 c. c. iod. sol. + 10 c. c.  $\text{CHCl}_3 = 22.6$  c. c.  $\text{Na}_2\text{S}_2\text{O}_3$

Iodine degree =  $\frac{12.3 \times 0.01265 \times 100}{0.355} = 43.8$

2. 0.303 gm. substance was treated with 20 c. c. iod. sol. and 10 c. c.  $\text{CHCl}_3$ ; 12.1 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  sol. were taken up by the excess of iodine.

Iodine degree =  $\frac{10.5 \times 0.01265 \times 100}{0.303} = 43.8$

Mean of the above two determinations = 43.8

But 1 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  was equal to (1-0.1) gm. iodine.

Corrected number = 39.4

The saponification equivalent for this sample of ghee was 218 (p. 66).

#### IODINE DEGREE FOR MUSTARD OIL.

(1) 0.140 gm. oil was digested for about 24 hours with 20 c. c. iod. sol. and 10 c. c. chloroform.

(2) 0.202 gm. oil was digested for the same length of time with 30 c. c. iod. sol. and 10 c. c.  $\text{CHCl}_3$ .

20 c. c. iod. sol. + 10 c. c.  $\text{CHCl}_3$  = 27.5 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  (Blank exp.)  
30 " " " " " " = 41.25 c. c. " "

(1) required 16.6 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  for the excess of iodine.

(2) " 25.4 " " " " " " " "

Amount of iodine consumed by (1) is equivalent to 10.9 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$ .

" " " (2) " " " " 15.85 c. c. "

Iodine degree for (1) =  $\frac{0.01265 \times 10.9 \times 100}{.14} = 98.5$

" " " (2) =  $\frac{0.01265 \times 15.85 \times 100}{0.202} = 98.5$

But 1 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  = 1 c. c.  $\text{I} \times \frac{10}{10.2}$  (as found by actual titration with pure iodine).

Iodine degree (corrected) = 96.9 or 97.0

#### IODINE DEGREE FOR NIGER-SEED OIL.

(1) 0.137 gm. oil was digested with 30 c. c. iod. sol. and 10 c. c. chloroform.

(2) 0.171 " " " 40 " " " " " "

(3) 0.098 " " " 30 " " " " " "

30 c. c.  $\text{I} + 10$  c. c.  $\text{CHCl}_3$  = 45.2 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  (Blank exp.)

Whence also

40 " " " = 60.26 " " "

(1) Required 32.0 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  for the excess of iodine.

(2) " 43.4 " " " " " " "

(3) " 35.6 " " " " " " "

Iodine degree for (1) =  $\frac{0.01265 \times 13.2 \times 100}{0.137} = 121.8$

" " (2) =  $\frac{0.01265 \times 16.86 \times 100}{.171} = 124.7$

" " (3) =  $\frac{0.01265 \times 9.6 \times 100}{0.098} = 123.9$

The *mean* of the three numbers is 123.5

$$\text{But } 1 \text{ c. c. Na}_2\text{S}_2\text{O}_3 = 1 \text{ c. c. } \frac{N}{10} \text{I} \times \frac{10}{10.3}$$

Hence the iodine degree (corrected) = 120

IODINE DEGREE FOR EARTH-NUT OIL.\*

(1) 0.181 gm. oil was digested with 20 c. c. iod. sol. and 10 c. c.  $\text{CHCl}_3$ .

20 c. c. I + 10 c. c.  $\text{CHCl}_3$  = 20.8 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  (Blank titration)  
4.7 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  were required for the excess of iodine.

$$\text{Iodine degree} = \frac{16.1 \times 0.01265 \times 100}{0.181} = 112.5$$

$$\text{But } 1 \text{ c. c. Na}_2\text{S}_2\text{O}_3 = 1 \text{ c. c. } \frac{N}{10} \text{I} \times \frac{10}{11.5}$$

$$\text{Corrected number} = 112.0 \times \frac{10}{11.5} = 97.5$$

(2) 0.1645 gm. oil was treated with 30 c. c. iod. sol. and 10 c. c. chloroform.

(3) 0.1535 " " " " 30 " " " "

(2) Required 15.0 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  for the excess of iodine.

(3) " 16.0 " " " " "

The iodine degree for (1) = 103.8

" " " (2) = 103.0

Mean of two determinations = 103.4

$$\text{But } 1 \text{ c. c. Na}_2\text{S}_2\text{O}_3 = 1 \text{ c. c. } \frac{N}{10} \text{I} \times \frac{10}{10.5}$$

$$\text{Hence corrected number} = 103.4 \times \frac{10}{10.5} = 98.5$$

MOWA FAT.

(1) 0.1815 gm. oil was treated with 10 c. c.  $\text{CHCl}_3$  and 20 c. c. iod. sol.

(2) 0.186 " " " " and 30 c. c. " "

11.5 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  were reqd. for the excess of iod. by (1)

21.5 " " " " " " (2)

20.0 c. c. iod. sol. + 10 c. c.  $\text{CHCl}_3$  = 20.6 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$

30.0 " " " " = 30.9 " "

From which we get the iodine degree for

(1) as 63.42, and that for (2) as 63.88

Mean of two = 63.7

$$\text{But } 1 \text{ c. c. Na}_2\text{S}_2\text{O}_3 = 1 \text{ c. c. } \frac{N}{10} \text{I} \times \frac{10}{10.3}$$

$$\text{Corrected number} = 63.7 \times \frac{10}{10.3} = 61.8$$

\* The saponification equivalent of this sample was found to be 195.0.



## IODINE DEGREE FOR SESAME' OIL.\*

(November 29, 1893.)

(1) 0.2806 gm. oil was digested with 20 c. c. iod. sol. and 10 c. c.  $\text{CHCl}_3$ .5.9 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  were required for the excess of iodine.20 c. c. I = 29.8 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  (Blank exp.)

$$\text{Iodine degree} = \frac{23.9 \times 0.01265 \times 100}{0.2806} = 107.7$$

But 1 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  had the actual strength 1 c. c.  $\times (1 - 0.02) \frac{N}{10}$  I

$$\text{Corrected number} = 107.7 (1 - 0.02) = 105.5$$

(December 5, 1893.)

(2) 0.1721 gm. oil was digested with 20 c. c. I sol. and 10 c. c.  $\text{CHCl}_3$ 

(3) 0.2065 " " " " " "

(4) 0.227 " " " " " "

20 c. c. I sol. + 10 c. c.  $\text{CHCl}_3$  = 25.5 c. c.  $\frac{N}{10}$   $\text{Na}_2\text{S}_2\text{O}_3$  (Blank titration)No. (2) required 10.9 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  for the excess of iodine.

No. (3) " 8.2 " " " " "

No. (4) " 6.4 " " " " "

From which we get the iodine degree for

$$\left. \begin{array}{l} (2) = 107.3 \\ (3) = 106.0 \\ (4) = 106.4 \end{array} \right\} \text{mean} = 106.6$$

But 1 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  = 1 c. c. I (1 - 0.02)

Corrected number = 106.6 (1 - 0.02) = 104.5.

## IODINE DEGREE FOR LARD.

(1) 0.2215 gm. lard was digested with 20 c. c. I and 10 c. c.  $\text{CHCl}_3$ 

(2) 0.1995 " " " " " "

15.1 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  were required by (1) for the excess of iodine

16.1 " " " " (2) " " "

20 c. c. I + 10 c. c.  $\text{CHCl}_3$  = 24.1 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  (Blank exp.)

$$\text{Iodine degree for (1)} = \frac{9 \times 0.01265 \times 10^2}{0.2215} = 51.4$$

$$\text{" " (2)} = \frac{8 \times 0.01265 \times 10^2}{0.1995} = 50.7$$

Mean of the two determinations = 51.0

But 1 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  = 1 c. c.  $\frac{N}{10}$  I  $\times (1 - 0.02)$ 

Whence corrected number = 50.0

\* The oil was extracted from the seeds by means of carbon bisulphide, and it was the same as used for determining the saponification equivalent.

## NOTE ON HÜBL'S IODINE ABSORPTION METHOD.

There is some difference of opinion as regards the excess of iodine, which should be present after its absorption. Thompson and Ballantyne, who have carefully revised the *constants* required in the analysis of some fats and oils, are of opinion that "at least double the amount of iodine absorbed should be present." Care was taken to fulfil this condition in most of the analyses as recorded above. On reference to sesamé and earth-nut oils, it would appear, however, that it is not always necessary that the iodine should be in large excess. Thus in one case the excess of iodine corresponds to only 5.9 c. c. N/10  $\text{Na}_2\text{S}_2\text{O}_3$  solution, and in another to only 4.7 c. c.  $\text{Na}_2\text{S}_2\text{O}_3$  solution without the results being discordant.

For convenience of reference the results obtained above are presented below in a tabulated form:—

*Table of constants in the analysis of fats and oils.*

NATURE OF FAT OR OIL.	Saponifica- tion equi- valent.	Glycerin per cent.	Iodine absorption.
Mustard oil ... ..	172-176	8.5	97.0
Niger-seed oil ... ..	190.0	10.8	120
Cocoanut oil ... ..	258.0	...	6.9
Ghee ... ..	218-222	...	33.5-39.4
Mowa fat ... ..	199.3	...	61.8
Mutton tallow ... ..	199.5-206	10.5	.....
Sesamé ... ..	189.9	...	104.5
Lard ... ..	195.4	...	50.0
Earth-nut oil ... ..	196.0	...	98.0

## SUMMARY AND CONCLUSION.

It would thus appear that as the saponification equivalents of niger-seed oil, mowa fat, mutton tallow, sesamé oil, lard and earth-nut oil are very close to one another, their admixtures in considerable proportions cannot be detected by Koettstorfer's test. Even the saponification equivalent of ghee is not far removed from that of lard or tallow. The saponification equivalents of mustard oil and cocoanut oil are, however, highly characteristic. The iodine degrees, on the other hand, afford us valuable hints as to the nature of adulteration, the most remarkable feature being the exceedingly low numbers for cocoanut oil and ghee. The results of the application of Reichert's test will be communicated later on.